

Ferro-electric phase transition in a polar liquid and the nature of λ -transition in supercooled water.

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We develop a series of approximations to calculate free energy of a polar liquid. We show that long range nature of dipole interactions between the molecules leads to para-electric state instability at low temperatures and to a second-order phase transition. We establish the transition temperature, T_C , both within mean field and ring diagrams approximation and show that the ferro-electric transition may play an important role explaining a number of peculiar properties of supercooled water, such as weak singularity of dielectric constant as well as to a large extent anomalous density behavior. Finally we discuss the role of fluctuations, shorter range forces and establish connections with phenomenological models of polar liquids.

Water is a major and all-important example of a strongly interacting polar liquid. Dielectric properties of water surrounding nano-scale objects pose a fundamentally important problem in physics, chemistry, structural biology and in silica drug design. The issue of temperature dependence of dielectric constant, the role of fluctuations and a possibility of a ferro-electric phase transition in a polar liquid is fairly old [1]. It attracted a new attention when a new phase transition (so called λ -transition) was observed in supercooled water at critical temperatures between $T_c = 228^0K$ [2, 3, 4] and $T_c = 231.4^0K$ [5]. Isothermal compressibility, density, diffusion coefficient, viscosity and static dielectric constant, ϵ , and other quantities show to a different degree singular behavior T_c is approached, which is signature of a phase transition. Phase behavior of such metastable water has been studied in a great detail by different authors a number of different but apparently interrelated theories where suggested. One popular view is given by the so called “stability limit conjecture”: thermodynamic anomalies arise from a single limit of mechanical stability (spinodal line), originating at the liquid-gas critical point [4, 6, 7]. Molecular dynamics shows that supercooling anomalies may be caused by a newly identified critical point, above which the two metastable amorphous phases of ice become indistinguishable [8]. In [9] the phase transition is explained as a formation of a rigid network of hydrogen bonds. On the other hand, the singularity of ϵ is a feature of a ferro-electric transition [10, 11]. A ferro-electric hypothesis was also proposed and supported by molecular-dynamics simulations (MD). For example, a ferro-electric liquid phase was observed in a model of the so called “soft spheres” with static dipole moments [12, 13, 14, 15]. In fact, the existence of a ferro-electric phase appears to be model independent: domains were formed both in MD calculations with hard spheres with point dipoles [13, 16] and with soft spheres with extended dipoles [17].

In this Letter we develop two related approaches to calculate free energy of a polar liquid. We show that long range nature of dipole interactions between the molecules leads to para-electric state instability at suf-

ficiently low temperatures and to a second-order phase transition. We establish the transition temperature, T_c , both within mean field and ring diagrams approximation and demonstrate that the ferro-electric transition is a sound physical explanation behind the experimentally observed λ -transition in supercooled water. Finally we discuss dielectric properties, the role of fluctuations and establish connections with earlier phenomenological models [18, 19] of polar liquids.

Let us start with potential energy of a model system of dipoles (molecules) located at positions \mathbf{r}_i and numbered $i = 1, 2, \dots, N$:

$$U = \frac{1}{2} \sum_{ij} u_{ij}. \quad (1)$$

The pair interactions u_{ij} between the molecules i and j forming the liquid can be modeled as

$$u_{ij} = \frac{f(r_{ij})d_0^2}{\epsilon_\infty} \sum_{\alpha, \beta} (\mathbf{S}_i)_\alpha (\mathbf{S}_j)_\beta [\delta_{\alpha\beta} - 3(\hat{\mathbf{r}}_{ij})_\alpha (\hat{\mathbf{r}}_{ij})_\beta], \quad (2)$$

where $r_{ij} = |\mathbf{r}_{ij}|$ stand for the vector separations between the molecules: $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, $\mathbf{d}_i = d_0 \mathbf{S}_i$ is the static dipole moment of a molecule i , d_0 is its absolute value and \mathbf{S}_i is the unit vector in the direction of the dipole moment (summation is assumed over repeated Cartesian indexes α and β). The function $f(r_{ij})$ represents the spatial dependence of the interaction between the molecules (see below). At last, ϵ_∞ is a dielectric constant of the liquid at frequencies exceeding rotational frequencies of the molecules. In fact ϵ_∞ stands for the electronic degrees of freedom polarization of the liquid molecules and thus is not directly included in Eq.(1).

At large distances $f(r_{ij}) \approx 1/r_{ij}^3$ as it should be for a dipole-dipole interaction. At smaller distances the interaction between the molecules is no longer described by its long-distance approximation (2). To account for the hydrogen bonding and other short-distance effects (here and on for the concreteness we should speak about water) without losing a possibility to perform analytical calculations we take the following, approximate, repre-

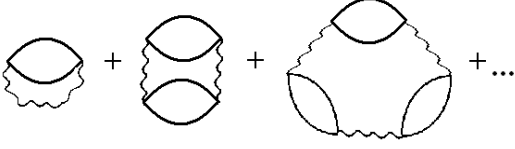


Figure 1: Ring diagrams approximation to free energy of an interacting system (5): Wavy lines and polarization loops represent electrostatic dipole-dipole interaction (2) and averaging over molecular degrees of freedom, respectively [25].

sensation for the intermolecular interaction:

$$f(r_{ij}) = \begin{cases} 1/r_{ij}^3, & r_{ij} > r_0 \\ 0, & r_{ij} \leq r_0 \end{cases},$$

where r_0 is model-dependent characteristic scale of interaction between molecules (see e.g. [20]). In spite of the simplicity of the suggested approximation for the intermolecular interaction, large scale properties of the liquid do not depend on exact value of r_0 (see below).

The dipole-dipole interaction falls faster with r_{ij} than the Coulomb one. Nevertheless it should be also considered as a long-range interaction. Indeed, let us consider the case of a uniformly polarized medium $\langle \mathbf{S}_i \rangle = \mathbf{s}(\mathbf{r}) = \text{const}$. Within the mean field approximation (MFA) the mean electric field at the position of the molecule i equals [21, 22, 23]

$$\mathbf{E}_M(\mathbf{r}_i) = \sum_j \frac{f(r_{ij})}{\epsilon_\infty} (\mathbf{d}_j - 3\hat{\mathbf{r}}_{ij}(\hat{\mathbf{r}}_{ij}, \mathbf{d}_j)) = \mathbf{E}_A + \mathbf{E}_P, \quad (3)$$

where $\mathbf{E}_A = 4\pi\mathbf{P}/3/\epsilon_\infty$ is the so called “action field”, $\mathbf{P} = P_0\mathbf{s}$ is the macroscopic polarization vector [21], and $P_0 = n_0 d_0$ (n_0 is the particle density of the liquid). \mathbf{E}_P is the polarization electric field produced by the polarization charges with a surface density $\sigma = P_n$, which may be as far away as on the sample surface.

The calculation of the free energy can be done with the help of thermodynamic integration: let us “switch on” the pair interaction between the molecules, $U \rightarrow \lambda U$, adiabatically by changing the scaling factor λ from 0 to 1. Then, the correlation energy, $F_{corr} = F - F_0$, where F_0 is the energy of the non-interaction system, can be obtained by the formal integration [24]:

$$F_{corr} = \int_0^1 d\lambda \langle U \rangle. \quad (4)$$

The averaging $\langle \dots \rangle$ here and everywhere below is assumed to be thermodynamic average over the Gibbs distribution:

$$\langle U \rangle = Z^{-1} \int d\gamma U \exp(-\lambda U/T),$$

where $d\gamma = \prod_i d^3 x_i d\Omega_{\mathbf{S}_i} / 4\pi V$, $Z = \int d\gamma \exp(-\lambda U/T)$, and V is the volume of the system ($n_0 V = N$).

As it is well known in plasma physics and will be further elucidated here for our dipole liquid example, MFA

to the free energy can be obtained with a help of the so called ring diagrams approximation (RA) [25], as shown on Figure 1:

$$\frac{\partial F}{\partial \lambda} = \sum_{n=0}^{\infty} \frac{\partial F^{(n)}}{\partial \lambda}, \quad (5)$$

where

$$\frac{\partial F^{(n)}}{\partial \lambda} = \frac{1}{2} \left(\frac{-\lambda}{T} \right)^n \sum_{i_1 \dots i_{n+1}} \int d\gamma_{i_1} \dots d\gamma_{i_{n+1}} u_{i_1 i_2} \dots u_{i_{n+1} i_1}. \quad (6)$$

Applying Fourier transform and integrating over directions $d\Omega_{\mathbf{S}}$ of the molecular dipole moments we find that

$$f(r)(\delta_{\alpha\beta} - 3\hat{r}_\alpha \hat{r}_\beta) = \int \frac{d^3 k}{(2\pi)^3} B(k) L_{\alpha\beta}(\hat{k}) \exp(i\mathbf{k}\mathbf{r}),$$

where $L_{\alpha\beta}(\hat{k}) = \delta_{\alpha\beta} - 3\hat{k}_\alpha \hat{k}_\beta$, and $B(k) = 4\pi(z \cos z - \sin z)/z^3$, we find, that:

$$\frac{\partial F^{(n)}}{\partial \lambda} = \frac{V}{2} \left(\frac{-\lambda}{T} \right)^n \left(\frac{d_0^2 N}{3\epsilon_\infty V} \right)^{n+1} \int \frac{dk^3}{(2\pi)^3} (B(k))^{n+1} Q_n,$$

where $Q_n = 2[1 - 2^n(-1)^n]$. The summation of all the ring diagrams and integration over λ finally lead to:

$$F_{corr} = T \int \frac{V d^3 k}{(2\pi)^3} \left[\ln \left(1 + \frac{n_0 d_0^2 B(k)}{3\epsilon_\infty T} \right) + \frac{1}{2} \ln \left(1 - \frac{2n_0 d_0^2 B(k)}{3\epsilon_\infty T} \right) \right]. \quad (7)$$

At $kr_D \ll 1$, $B(k) \approx -4\pi/3 + 2\pi(kr_0)^2/15$, and the first term in Eq. (7) takes the form:

$$F_{corr}^{(1)} = T \int \frac{V d^3 k}{(2\pi)^3} \ln \left(1 - \frac{T_c}{T} + \gamma(kr_0)^2 \right), \quad (8)$$

where $\gamma = 1/10$ and

$$T_c = \frac{4\pi n_0 d_0^2}{9\epsilon_\infty}. \quad (9)$$

Of course, the parameter γ is model-dependent, and depends on the details of short-range interactions between the molecules. Although its value for a specific liquid is not really known, we expect $\gamma \sim 1$ (see the connection to a polar liquid phenomenology below).

Free energy (8) of the liquid has a meaning only at sufficiently high temperatures: $\tau = (T - T_c)/T_c > 0$. At $T < T_c$ the free energy (8) becomes singular, the para-electric phase ($\mathbf{s} = 0$) becomes unstable and a ferro-electric phase transition takes place at $T = T_c$.

Below the phase transition, at $T < T_c$, a simpler approach can be taken. Indeed in thermodynamic equilibrium the density of polarization charges vanishes: $\rho_P = -\nabla \mathbf{P} = 0$ due to the formation of a domains (see [26])

and, therefore, $\mathbf{E}_P = 0$ as well. Let us neglect fluctuations first and consider a polarized state of a liquid with $\mathbf{E}_P = 0$. Then, the energy of the liquid is

$$U = \frac{1}{2} \sum_i \mathbf{d}_i \mathbf{E}_M(\mathbf{r}_i) = -\frac{2\pi n_0 d_0^2 N s^2}{3\epsilon_\infty}. \quad (10)$$

In the vicinity of the phase transition, $|\tau| \ll 1$, the polarization of the liquid is small: $s \ll 1$. One-particle distribution function for the molecular dipoles orientation has the form: $f(\theta) = (1 + 3s \cos \theta)/4\pi$, where θ is the angle between vectors \mathbf{S} and \mathbf{s} . Then $\langle s_z \rangle = s$ and entropy of the liquid is:

$$S = -N \int d\Omega \mathbf{s} f \ln f \approx -\frac{3}{2} N s^2 - \frac{1}{15} N s^4.$$

Combining the above expressions we obtain the following representation of the non-equilibrium free energy

$$F(\mathbf{s}) = U - TS = a s^2 + b s^4, \quad (11)$$

where $a = 3N(T - T_c)/2$ and $b = NT_c/15$. The free energy (11) has the Landau form [24], suggesting the phase transition is of the second order at $T = T_c$.

In a weak electric field \mathbf{E} the free energy is $F \approx a s^2 - Nd_0 \mathbf{s} \mathbf{E} - Nd_e \mathbf{E}$, where $\mathbf{d}_e = (\epsilon_\infty - 1)\mathbf{E}/4\pi n_0$ is the induced electronic dipole moment of the molecules. At $T > T_c$ the minimization of F gives $\mathbf{s} = \mathbf{E} d_0 / 3T_c \tau$. Therefore the static dielectric constant is given by:

$$\epsilon = \epsilon_\infty \left(1 + \frac{3T_c}{T - T_c} \right) \quad (12)$$

and diverges at $T = T_c$. There are a few measurements of ϵ_∞ for water: $\epsilon_\infty \approx 4.9$ [27] and $\epsilon_\infty = 5.5$ [28]. Plugging the experimental values into Eq. (9) we obtain: $T_c = 236^0 K$ and $T_c = 210^0 K$, respectively. The second order phase transition was indeed observed in the supercooled water at $228^0 K$ ("the λ -transition" [2, 3, 4]), which is in a good agreement with our findings.

At $T \rightarrow T_c + 0$ such values as isothermal compressibility, density, diffusion coefficient of the molecule, viscosity and static dielectric constant ϵ diverge. The singularity of ϵ led to ferro-electric phase transition hypotheses [10, 11]. Eq. (12) shows that ϵ diverges as $\epsilon \propto |\tau|^{-1}$. According to the experiments $\epsilon \propto |\tau|^{-0.13}$ [3]. The reason of the discrepancy should be contributed to MFA failure in the direct vicinity of the transition. At $T = 0^0 C$ depending on the accepted value of ϵ_∞ we obtain $\epsilon = 99$ and $\epsilon = 61$, respectively, both close the observed value $\epsilon = 88$ [27].

Finally let us connect our MFA model with polar liquid phenomenology [18]. Consider a more general case, $\mathbf{E}_P \neq \mathbf{0}$, $\mathbf{s}(\mathbf{r}) \neq \text{const}$, $s \ll 1$. Then, instead of Eq. (10) we obtain:

$$U = \frac{1}{2} \sum_{i \neq j} u_{ij} = -\frac{1}{2} \sum_i \mathbf{d}_i (\mathbf{E}_A(\mathbf{r}_i) + \mathbf{E}_P(\mathbf{r}_i)).$$

Taking into account Poisson equation, $\Delta \phi_P = -4\pi \rho_P / \epsilon_\infty$, the definition for the density of polarization

charges, $\rho_P = -P_0 \text{divs}$, and the electrostatic potential, $\mathbf{E}_P = -\nabla \phi_P$, we obtain:

$$U = \int dV \left(-\frac{2\pi P_0^2}{3\epsilon_\infty} s^2(\mathbf{r}) + \frac{\epsilon_\infty \mathbf{E}^2_P}{8\pi} \right).$$

The entropy of the liquid can be expressed as

$$S = n_0 \int dV \left(-\frac{3}{2} s^2(\mathbf{r}) - \frac{1}{15} s^4(\mathbf{r}) \right).$$

Transition from homogeneous to inhomogeneous polarization cases means the deformation of hydrogen bonds. Therefore, the MFA free energy of the liquid should allow additional Oseen like positive " H -bonding" term (see e.g. [18, 24])

$$F[\mathbf{s}] = \int dV \left[\frac{P_0^2}{2} \left(C \sum_{\alpha, \beta} \frac{\partial s_\alpha}{\partial x_\beta} \frac{\partial s_\alpha}{\partial x_\beta} + V(s^2) \right) + \frac{\epsilon_\infty \mathbf{E}^2_P}{8\pi} \right], \quad (13)$$

where C is the phenomenological parameter responsible for the h-bonds network rigidity, $V(s^2 \ll 1) \approx A s^2/2 + B s^4$, and $A = 4\pi\tau/3\epsilon_\infty$, $B = 4\pi/135\epsilon_\infty$.

Eq. (13) with a general potential $V(s^2)$ can be considered as a phenomenological free energy of a polar liquid. At $s \sim 1$ the function takes into account the short-range part of the intermolecular interaction potential and thus depends on details of interactions of individual molecules. Asymptotically $V'(s^2 \rightarrow 1) \rightarrow \infty$ [18], although the exact shape of $V(s^2)$ can only be established either from experiments or detailed MD studies.

Next to the phase transition, $|\tau| \ll 1$, fluctuations become essential. The free energy of a liquid can be obtained in a usual way [24]:

$$F = -T \ln \left[\int D\mathbf{s}(\mathbf{r}) \exp \left(-\frac{F(\mathbf{s}(\mathbf{r}))}{T} \right) \right], \quad (14)$$

i.e. as a result of averaging over fluctuations. Neglecting the nonlinear part of $V(s^2)$ and Fourier transforming the functional (13) we find that

$$F[\mathbf{s}] = \frac{P_0^2}{2} \sum_{\mathbf{k}} \left[(Ck^2 + A) |\mathbf{s}_{\mathbf{k}}|^2 + 4\pi |\hat{\mathbf{k}} \hat{\mathbf{s}}_{\mathbf{k}}|^2 \right].$$

The integration in (14) is then straightforward and gives:

$$F = VT \int \frac{d^3 k}{(2\pi)^3} \ln \left(1 - \frac{T_c}{T} + \frac{3\epsilon_\infty C}{4\pi} k^2 \right) + \text{const.} \quad (15)$$

The latter expression should be compared with Eqs. (7) and (8) obtained within the ring approximation. Since Eqs. (8) and (15) have the same form, we imply that averaging in RA represents averaging over fluctuations on top of MFA thermal state. Moreover we establish the relation between the model-dependent "microscopic" cutoff parameter r_0 used in RA and the phenomenological constant C : $\gamma r_0^2 = 3\epsilon_\infty C / 4\pi$.

The water density maximum at $T = 4^\circ\text{C}$ [10, 29, 30, 31] is often related to supercooled anomalies as well [32]. Let us show that this density behavior in our model originates from the dipole field fluctuations in the vicinity of the ferro-electric transition. Consider the liquid approaching the phase transition from above: $\tau \ll 1$, $T > T_c$. In the region where the fluctuations are still small, $s \ll 1$, the complete Free energy takes form:

$$F = \int dV d_0^2 n^2 \left[\frac{C}{2} (\nabla_\alpha s_\beta)^2 + V(s) \right] + \int dV \frac{\beta}{2} (n')^2 \quad (16)$$

where $n'(\mathbf{r}) = n(\mathbf{r}) - n_0$ represent the density fluctuations, $\beta = mC_S^2/n_0$, m is the mass of the molecule, C_S is the speed of a sound. Since the most important contribution to F comes from the long wave length fluctuations of \mathbf{s} , the vector field \mathbf{s} is slow variable and therefore the density can be found by the minimization of the free energy at a given value of \mathbf{s} :

$$n' = -\frac{P_0^2}{n_0\beta} \left[C (\nabla_\alpha s_\beta)^2 + As^2 + 2Bs^4 \right]. \quad (17)$$

Averaging over the polarization field fluctuations we find that $\langle n' \rangle = n_1 + n_2$, n_1 practically does not depend on T , and the temperature dependence is contained in n_2 :

$$\langle n' \rangle = \text{const} + n_0 D \sqrt{\tau}, \quad (18)$$

where $D = \xi Q$, $Q = BT^2 k_{max} \epsilon_\infty^2 / mC_S^2 P_0^2 R_D^5 \sim 1$, and $R_D = \sqrt{C\epsilon_\infty/4\pi}$ is the correlation radius introduced in [18]. R_D is roughly a size of a tightly correlated domain of molecular dipoles and plays the role similar to Debye radius in plasma models. The factor $\xi = 5(2\pi)^{-5}/\sqrt{3} \ll 1$ so that D appears to be small. In fact the smallness of ξ is the defect of the mean field theory and in a full theory of the phase transition taking into account the scale invariant fluctuations of the order parameter $\xi \sim 1$, as shown in [33, 34]. Eq. (18) shows that the density of the

liquid drops near the phase transition point. At larger temperatures the density decreases due to a normal thermal expansion of the liquid. Therefore complete model predicts maximum density at a certain temperature.

Fluctuations in a homogeneous liquid become important when $C_{FL} = -T\partial^2 F/\partial T^2 \gtrsim \Delta C$ [33, 35], where C and ΔC are heat capacity and the jump of the heat capacity at $T = T_c$. The application of this condition to the model (15) gives the following range of fluctuation region: $|\tau| \lesssim 1/z^2$, where $z = 4\pi n_0 R_D^3/3$. For water we have $R_D \sim 0.3\text{nm}$ and $z \sim 4$. This means the phenomenological (MFA) free energy (13) can be applied at $T \gtrsim -20^\circ\text{C}$. The mean field approach is applicable, since the number of particles within R_D is large: $z \approx 4 \gtrsim 1$.

The combination of RA and MFA approaches together with the established connection with polar liquid phenomenology explains a number of important features behind the phase transition observed in supercooled water at $T \approx -45^\circ\text{C}$ [2, 3, 4, 5]. The ‘‘gaseous parameter’’ z for water is not very large, which means that MFA approach to the phase transition developed here can not explain every experimental or MD feature in a realistic situation. Although our approximation (9) for T_c and (12) for the dielectric constant turns out to be fairly good and appear to capture all the important physics, calculations of quantities such as critical exponents near T_c should require a more complete theory including all the details of short-distance hydrogen-bonds network formation [9, 11, 36] as well as scale invariant character of order parameter fluctuations in the vicinity of the phase transition [24]. In any case we believe that long range dipole-dipole interaction of molecules plays a key role in explaining supercooled water anomalies and interactions in aqueous environments [18, 19].

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